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(54) **Detergent compositions**

(57) There is provided a detergent composition containing:

- (a) a source of peroxide compounds
- (b) a peroxyacid bleach precursor composition comprising

- i) an organic peroxyacid bleach precursor compound,
- ii) an H_2O_2 scavenging material,

wherein said organic peroxyacid bleach precursor compound and said H_2O_2 scavenging material are in close physical proximity within said composition.

The composition is useful in the bleaching of stains from stained coloured fabrics. The H_2O_2 scavenging material acts to inhibit 'patchy' fabric discolouration to said fabrics during the stain bleaching process.

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Description

Technical field

5 This invention relates to detergent compositions containing a source of hydrogen peroxide and a peroxyacid bleach precursor composition. More particularly, it relates to an H_2O_2 scavenging material containing peroxyacid bleach precursor composition within a detergent composition.

Background to the invention

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The satisfactory removal of bleachable soils/stains such as tea, fruit juice and coloured vegetable soils from stained fabrics is a particular challenge to the formulator of a bleaching composition for use in a laundry washing method. Traditionally, the removal of such bleachable stains has been facilitated by the use of bleach components such as oxygen bleaches, including hydrogen peroxide and organic peroxyacids. The organic peroxyacids are often obtained by the in situ perhydrolysis reaction between hydrogen peroxide and an organic peroxyacid bleach precursor.

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The growth in usage of organic peroxyacid bleach precursors has mirrored a decrease in fabric wash temperatures which itself has accompanied an increase in the proportion of fabrics that are coloured. One problem that has become more significant as a result of these trends is that of "patchy" localised discolouration to fabric colours and materials caused by the development of localised high concentrations of bleaching species. High transient concentrations can arise for several reasons. The bleaching species may itself have an intrinsically low solubility, its solubility may have been hindered by the presence of other materials such as viscous surfactant phases or the agitation regime in the immediate environment of the bleach species may not be high enough to disperse the dissolved bleach. Where a peroxyacid bleach precursor forms a component of the composition the potential problem is increased. In addition to the potential for localised high concentrations of perhydroxyl ion arising from dissolution of the inorganic perhydrate normally contained in laundry detergent compositions, the perhydrolysis of the peroxyacid bleach precursor can give rise to significant localised peroxyacid bleach concentrations. This is especially true when the detergent composition contains high levels (for example, greater than 3% by weight) of the peroxyacid bleach precursor compound and/or when sodium percarbonate is used as the source of hydrogen peroxide.

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The Applicants have found that the problem of 'patchy' discolouration can be particularly troublesome with peroxyacid bleach precursor compounds which on perhydrolysis provide a peroxyacid which is a perbenzoic acid, or non-cationic substituted derivative thereof, or a cationic peroxyacid. Precursor compounds of the benzoxazin type, in particular, have also been found to give rise to the problem.

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The development of so-called concentrated products and their delivery via dispensing devices placed in the machine drum together with the fabric load has merely served to exacerbate these problems.

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Accordingly a need exists to provide detergent compositions in which the organic peroxyacid bleach precursor is incorporated in a form that minimises and preferably eliminates patchy discolouration of fabric colours during its dissolution and perhydrolysis in the wash liquor, whilst still providing acceptable bleachable soil/stain removal from soiled/stained fabrics.

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The prior art contains numerous examples of organic peroxyacid bleach precursors coated or agglomerated so as to increase their stability on storage in detergent compositions and/or to influence their solution behaviour.

EP-A-0070474 discloses granulate organic peroxyacid bleach precursors prepared by spray drying an aqueous pumpable dispersion containing an N-acyl or O-acyl compound together with at least one water soluble cellulose ether, starch or starch derivative in a weight ratio of activator to coating of from 98:2 to 90:10.

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GB-A-1507312 discloses the coating of organic peroxyacid bleach precursors with a mixture of alkali metal $C_8 - C_{22}$ fatty acid salts in admixture with the corresponding fatty acids. GB-A-1381121 employs a molten coating of inter alia $C_{14} - C_{18}$ fatty acid mixtures to protect solid organic peroxyacid bleach precursors. GB-A-1441416 discloses a similar process employing a mixture of $C_{12} - C_{14}$ fatty acids and $C_{10} - C_{20}$ aliphatic alcohols. EP-A-0375241 describes stabilised organic peroxyacid bleach precursor extrudates in which $C_5 - C_{18}$ alkyl peroxy carboxylic acid precursors are mixed with a binder selected from anionic and nonionic surfactants, film forming polymers fatty acids or mixtures of such binders.

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EP-A-0356700 discloses compositions comprising an organic peroxyacid bleach precursor, a water soluble film forming polymer and 2-15% of a $C_3 - C_8$ polyvalent carboxylic acid or hydroxycarboxylic acid for enhanced stability and ease of dispersion/solubility. The carboxylic acid, of which a preferred example is citric acid, is dry mixed with the organic peroxyacid bleach precursor and then granulated with the film forming polymer. The citric acid is asserted to provide an enhanced rate of dissolution of the organic peroxyacid bleach precursor granules.

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EP-A-0382464 concerns a process for coating or encapsulation of solid particles including bleaching compounds and organic peroxyacid bleach precursors in which a melt is formed of coating material in which the particles form a disperse phase, the melt is destabilised and then caused to crumble to a particulate material in which the disperse phase particles are embedded in the continuous (coating) phase. A variety of coating materials are disclosed and certain

materials such as polyacrylic acid and cellulose acetate phthalate are taught as being useful where release of the coated material is dependent on pH.

The overall emphasis in the prior art has thus been on the protection of the organic peroxyacid bleach precursor against a hostile environment during storage and relatively little attention has been paid to the dissolution characteristics of the coated or agglomerated material in use. Where coating and/or agglomeration has been proposed with poorly soluble materials such as fatty acids, this has resulted in a rate of perhydrolysis of the organic peroxyacid bleach precursor which is slower than that which would occur if it had not been so protected, thereby reducing the effectiveness of the resultant peroxycarboxylic acid bleach. Any use of more rapidly soluble materials such as citric acid has been in the context of an agglomerate component in which more rapid solution of the organic peroxyacid bleach precursor has been the objective. Another approach for solving the problem of fabric damage is given in JP57296 wherein a water-insoluble mineral substance, a peroxyacid bleach precursor and a bleach compound are mixed together in a ratio of said mineral substance to said precursor and bleach compound of 1:99 to 90:10, preferably 20:80 to 65:35. The water-insoluble mineral substance is selected from acid clay, activated clay, kaolin, bentonite, diatomaceous earth and perlite, and is said to inhibit fading without inhibiting the bleaching action. EP028432 is concerned with 'pinpoint damage' to fabrics which produces small and localised area of damage (usually not more than 2 to 5mm in diameter) on the fabric due to a slow dissolution of the bleach system. Said document discloses a granule containing detergent composition comprising from 5% to 80% of a peroxyacid bleach precursor, from 15% to 60% of a water-insoluble silicate and 5% to 40% of a nonionic binder within a solid detergent composition. This water-insoluble silicate compound, of which a smectite clay is preferred, is mixed with the peroxyacid bleach precursor and further bound with the nonionic surfactant. This combination is asserted to provide a rapid generation of peroxycarboxyl anions when added to a source of hydrogen peroxide. In any instances, because perhydrolysis commences as soon as the detergent product starts to dissolve and form an alkaline hydrogen peroxide environment the problem of localised peroxy acid bleach concentrations has remained unsolved.

One solution to this problem would be to delay the start of perhydrolysis in order to avoid the fabric colour damage problems associated with the dissolution behaviour of other detergent products components. An exemplary disclosure is given in WO92/13798, where acidic materials having specified characteristics can be used as coating materials for peroxyacid bleach precursors to delay the onset of perhydrolysis during the initial stages of dissolution/dispersion of the product in the aqueous wash pre-liquor.

However, compositions containing such acidic coating materials are expensive and require complex processes. Furthermore, the fabric colour damage prevention has been found to be limited in presence of high levels of peroxyacid bleach precursors.

The Applicants have now surprisingly found that the problem of 'patchy' fabric discolouration, can be significantly reduced by the close physical proximity of an H_2O_2 scavenging material and the organic peroxyacid bleach precursor containing bleach precursor composition. The inclusion of the H_2O_2 scavenging material has also been found not to significantly compromise the release of the peroxyacid in the wash liquor as well as the bleachable stain removal ability of the composition.

In addition, the provision of an H_2O_2 scavenging material in close physical proximity with an organic peroxyacid bleach precursor within a bleach precursor composition has been found to enhance the storage stability of said precursor material.

By close physical proximity, it is meant an agglomerate or extrudate in which said H_2O_2 scavenging material and said organic peroxyacid bleach precursor are in intimate admixture. It may also mean a bleach precursor particle coated with at least one layer wherein at least one layer contains the H_2O_2 scavenging material. It has to be understood by close proximity that the scavenging material and the peroxyacid bleach precursor are not two separate discrete particles in the detergent composition.

For the purposes of the present invention, the H_2O_2 scavenging material, contained in a peroxyacid bleach precursor composition within a detergent composition, is defined as follows:

An H_2O_2 scavenging material is a compound which reduces the level of H_2O_2 produced by a source of active oxygen in an aqueous wash pre-liquor by reacting with said H_2O_2 via any of the following processes: decomposition, neutralisation and adsorption, and any combination thereof and which does not ultimately form an organic peroxyacid compound.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the Invention

According to the present invention there is provided a detergent composition containing:

(a) a source of peroxide compounds

(b) a peroxyacid bleach precursor composition comprising

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i) an organic peroxyacid bleach precursor compound,

ii) an H_2O_2 scavenging material,

wherein said organic peroxyacid bleach precursor compound and said H_2O_2 scavenging material are in close physical proximity within said composition.

Preferably, said organic peroxyacid bleach precursor compound and said H_2O_2 scavenging material are in close contact, most preferably in intimate admixture within said bleach precursor composition.

The H_2O_2 scavenging material is selected from compounds reacting with H_2O_2 via a decomposition, and/or neutralisation, and/or adsorption process.

Preferred H_2O_2 scavenging materials are selected from a decomposition process, namely Heavy Metal Ions (HMI) and enzymes of the catalase and peroxidase type.

Also provided herein is a process for producing a detergent composition according to the invention and comprising the steps of:

- a)-preparing a peroxyacid bleach precursor agglomerate by mixing an organic peroxyacid bleach precursor compound with an H_2O_2 scavenging material, to which is thereafter mixed a binder material,
- b)-treating said agglomerates with a coating material,
- c)-drying said coated agglomerates, and
- d)-incorporating said dried coated agglomerates in a detergent composition containing a source of peroxide compounds.

Detailed description of the invention

An essential feature of the invention is a source of peroxide compounds combined with a peroxyacid bleach precursor composition within a detergent composition. A preferred peroxide compound is hydrogen peroxide. Preferred sources of hydrogen peroxide include percarbonate and perborate. Sources of peroxide compound include also inorganic perhydrate bleaches, perphosphate, persulfate and persilicate bleaches.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the metal salt, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the detergent compositions.

Examples of inorganic perhydrate salts include perborate and percarbonate. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilise a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2 \cdot H_2O_2$ or the tetrahydrate $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$.

Sodium percarbonate, which is a preferred perhydrate for inclusion in compositions in accordance with the invention, is an addition compound having a formula corresponding to $2Na_2CO_3 \cdot 3H_2O_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in product stability.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interlox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4 \cdot n \cdot Na_2CO_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Other non-limiting examples of coatings which contain silicate (alone or with borate salts or boric acids or other inorganics), waxes, oils, fatty soaps can also be used advantageously within the present invention.

Peroxyacid bleach precursor composition

The peroxyacid bleach precursor composition comprises as essential components an organic peroxyacid bleach precursor and an H_2O_2 scavenging material.

Organic peroxyacid bleach precursor

The compositions in accordance with the present invention also include peroxyacid bleach precursors (bleach activators). The peroxyacid bleach precursors are normally incorporated at a level of from 30% to 95% by weight of the bleach precursor composition, preferably at least 55% and most preferably at least 60% by weight thereof. In absolute terms the peroxyacid bleach precursor is typically from 1% to 20% by weight, more preferably from 1% to 10% by weight, most preferably from 1% to 7% by weight of the detergent compositions.

Peroxyacid bleach precursors for inclusion in the composition in accordance with the invention typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, nitriles and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789.

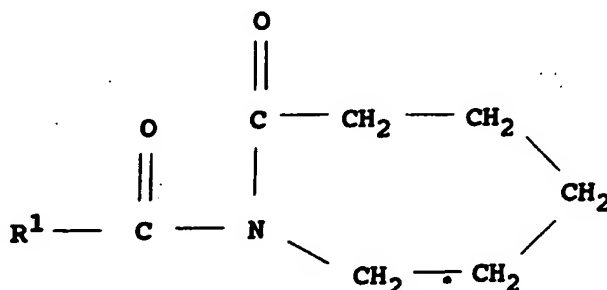
Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386. The acylation products of sorbitol, glucose and all saccharides with benzoylating agents and acetylating agents are also suitable.

Specific O-acylated precursor compounds include 3,5,5-tri-methyl hexanoyl oxybenzene sulfonates, benzoyl oxybenzene sulfonates, cationic derivatives of the benzoyl oxybenzene sulfonates, nonanoyl-6-amino caproyl oxybenzene sulfonates, monobenzoyltetraacetyl glucose and pentaacetyl glucose. Phthalic anhydride is a suitable anhydride type precursor. Useful N-acyl compounds are disclosed in GB-A-855735, 907356 and GB-A-1246338.

Preferred precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine, N-benzoyl substituted ureas and the N,N,N',N' tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. A most preferred precursor compound is N,N,N',N' tetra acetyl ethylene diamine (TAED).

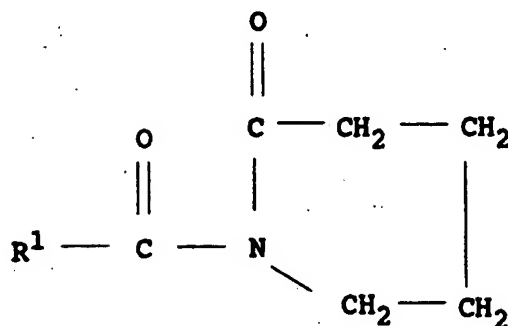
N-acylated precursor compounds of the lactam class are disclosed generally in GB-A-955735. Whilst the broadest aspect of the invention contemplates the use of any lactam useful as a peroxyacid precursor, preferred materials comprise the caprolactams and valerolactams.

Suitable caprolactam bleach precursors are of the formula:



wherein R¹ is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms.

Suitable valero lactams have the formula:

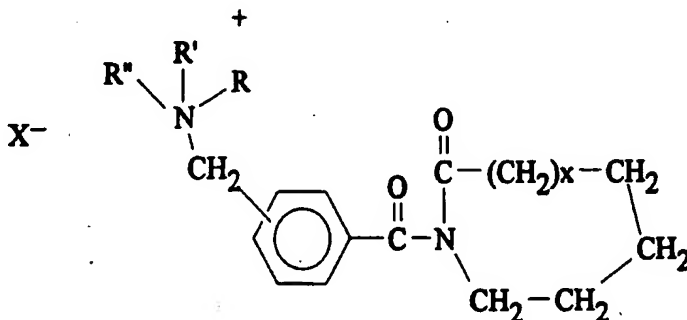


wherein R¹ is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R¹ is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

The most preferred materials are those which are normally solid at $<30^{\circ}\text{C}$, particularly the phenyl derivatives, ie. benzoyl valerolactam, benzoyl caprolactam and their substituted benzoyl analogues such as chloro, amino, nitro, alkyl, alkyl, aryl and alkoxy derivatives.

Caprolactam and valerolactam precursor materials wherein the R¹ moiety contains at least 6, preferably from 6 to about 12, carbon atoms provide peroxyacids on perhydrolysis of a hydrophobic character which afford nucleophilic and body soil clean-up. Precursor compounds wherein R¹ comprises from 1 to 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of 'hydrophobic' and 'hydrophilic' caprolactams and valero lactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

Another preferred class of bleach precursor materials include the cationic bleach activators, derived from the valerolactam and acyl caprolactam compounds, of formula:



wherein x is 0 or 1, substituents R, R' and R'' are each C1-C10 alkyl or C2-C4 hydroxy alkyl groups, or $[(C_2H_5)_O]_n-R'''$ wherein y=2-4, n=1-20 and R''' is a C1-C4 alkyl group or hydrogen and X is an anion.

Suitable imidazoles include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing peroxyacid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:

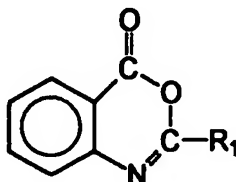


wherein R¹ is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing

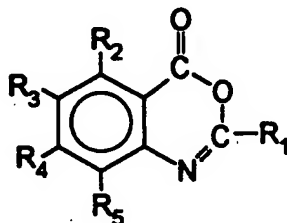
1 to 10 carbon atoms and L can be essentially any leaving group. R¹ preferably contains from about 6 to 12 carbon atoms. R² preferably contains from about 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should preferably not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Benzoaxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoaxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

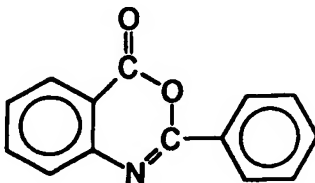


including the substituted benzoaxazins of the type



wherein R₁ is H, alkyl, alkaryl, aryl, arylalkyl, secondary or tertiary amines and wherein R₂, R₃, R₄, and R₅ may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkyl amino, COOR₆ (wherein R₆ is H or an alkyl group) and carbonyl functions.

An especially preferred precursor of the benzoaxazin-type is:



H₂O₂ scavenging material

The bleach precursor compositions useful for the purpose of the invention contain a H₂O₂ scavenging material. In an essential aspect, the H₂O₂ scavenging material and the organic peroxyacid bleach precursor compound are in close physical proximity, more preferably in close contact, most preferably in intimate admixture within said composition to form a bleach precursor particulate.

The H₂O₂ scavenging material is selected from compounds which react with H₂O₂ via a decomposition, neutralisation or adsorption process or any combination thereof.

H₂O₂ Scavenger compounds reacting with a decomposition process

Suitable compounds, for the purpose of the invention, which react with H₂O₂ via a decomposition process are selected from Heavy Metal Ions, catalase enzymes, peroxidase enzymes and nitroso compounds or any mixtures thereof.

Heavy Metal Ions (HMI)

HMI may be present within the precursor composition as salts per se, in a metal oxide form or carried by a mineral compound.

When HMI as salts per se are used in the bleaching composition it is preferred to include separately a heavy metal ion sequestrant in the detergent composition which will sequester the HMI, especially after the first stages of dissolution/dispersion of the peroxide bleach precursor. Preferably, this heavy metal ion sequestrant as described hereinafter will be present in the detergent composition in molar excess of the HMI.

A preferred H₂O₂ scavenging material is an heavy metal ion (HMI) present within the precursor composition at levels less than 5% by weight, preferably less than 1% by weight and more preferably less than 0.1% by weight of the bleach precursor composition.

These HMI are selected from elements contained in the third and fourth rows of the third to the twelfth columns of the periodic table.

Preferred HMI are Fe, Cu and Mn. The level of Iron, Copper and Manganese in the bleaching composition should be less than 5000ppm, preferably 1000 ppm. In particular, the level of Copper should be less than 50ppm.

HMI may also be carried by mineral compounds. Suitable carrier materials for HMI are mineral materials which contain at least 200 ppm or HMI and preferably at least 500 ppm.

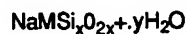
A possible carrier material is a non-three dimensional phyllosilicate mineral material.

The non-three dimensional phyllosilicate mineral material is preferably present such that the weight ratio of the non-three dimensional phyllosilicate mineral material to organic peroxyacid/bleach precursor compound or said preformed organic peroxyacid in the bleaching composition is from 1:1 to 1:99, preferably from 1:2 to 1:49, more preferably from 1:3.5 to 1:19.

By non-three dimensional phyllosilicate mineral material it is meant herein a silicate mineral material in which essentially flat (two dimensional) sheets are formed by the sharing of three of the four oxygen atoms in each silicate tetrahedron with neighbouring tetrahedrons. This definition excludes those silicates having a more complex three dimensional silicate linking structure which are occasionally referred to as "framework minerals". Preferred non-three dimensional phyllosilicate mineral materials herein include clay mineral materials and the crystalline layered silicates. For clarity, it is noted that the term non-three dimensional phyllosilicate mineral material, as used herein excludes sodium aluminosilicate zeolite builder compounds, which however, may be included in the detergent compositions of the invention as optional builder components.

The non-three dimensional phyllosilicate mineral material is preferably present as a component of an agglomerate particle containing the organic peroxyacid bleach precursor compound, and optionally other detergent compounds, including polymeric organic binders.

Suitable carriers include crystalline layered silicates which have the general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0 164 514 and methods for their preparation are disclosed in DE-A-3 417 649 and DE-A-3 742 043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2.

The most preferred material is $\delta\text{-Na}_2\text{Si}_2\text{O}_5$, available from Hoechst AG as NaSKS-6.

The crystalline layered silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof.

Enzymes as H₂O₂ scavenging materials

Still another preferred H₂O₂ scavenging material with a H₂O₂ decomposition process is an enzyme of the catalase type. This enzyme, also called heme-enzyme, catalyses the decomposition of hydrogen peroxide to water and oxygen, so that 1mg of enzyme decomposes at least 0.1 mmol of H₂O₂/min at pH 7 and 25°C, and is found in animal, plant cells, bacteria and fungi. Said catalase contains four tetrahedrally arranged sub-unit of equal size giving an approximate molecular weight of 240,000. Each subunits consists of a single polypeptide chain associated with a single prosthetic group ferric protoporphyrin IX. Catalases are usually incorporated to the bleach precursor composition at levels less than 5%, preferably 1% by weight of the precursor composition.

Preferred catalases are Terminox® sold by NOVO Industries A/S and Fermocolase® sold by Finnsugar.

Peroxidase enzyme as H₂O₂ scavenger are also suitable. Peroxidase enzyme include for example horseradish peroxidase, ligninase, and haloperoxidase such as chloro and bromo-peroxidase. When used, this enzyme will usually be incorporated to the bleach precursor composition at levels less than 5%, preferably less than 1% by weight of the precursor composition.

Another suitable compound as an H₂O₂ scavenger with a decomposition process is a nitrosocompound such as nitrosodimethylaniline.

H₂O₂ scavenger compounds reacting with a neutralisation process

Suitable compounds, for the purpose of the invention, which react with H₂O₂ by neutralising said H₂O₂ are selected from the non-limiting list:

1. halogen compounds of formula Mx wherein M is a metal and x a halogen selected from Cl, Br and I
2. Sulphite compounds (sodium sulphite or sodium hydrogen sulphite)
3. thiosulfates
4. thiols, of which thiourea and thioglycerol are preferred
5. ascorbic acid
6. tertiary amines, of which nitrite triacetic acid is preferred
7. sodium hypochlorite
8. sodium triolybdate
9. glyoxylic acid
10. N-acetyl cysteine
11. Sulphide compounds
12. Barium hydroxide

When used, such compounds will be incorporated in the bleach precursor composition as levels of less than 10%, preferably less than 5% by weight of the bleach precursor composition.

H₂O₂ scavenger compounds reacting with an adsorption process

Suitable H₂O₂ scavenger compounds, which react with H₂O₂ by an absorption process are these compounds selected from: activated charcoals specifically NH₃ activated charcoals, dust and sand.

When used such compound will be incorporated in the bleach precursor composition at levels less than 50%, preferably less than 20% by weight of the bleach precursor composition.

Mixtures of any of the H₂O₂ scavenger herein before described may be used.

Preferred H₂O₂ scavenger compounds suitable for the purpose of the invention are those which react with H₂O₂ by decomposing it. More preferably, these compounds are selected from heavy metal ions and enzymes of the catalase type.

The incorporation of other ingredients additional to the organic peroxyacid bleach precursor compound and H₂O₂ scavenging material can be advantageous particularly in the processing of the bleach precursor particulates and also in enhancing the stability of detergent compositions in which the particulates are included. In particular, certain types of agglomerates may require the addition of one or more binder agents in order to assist in binding the organic peroxyacid bleach precursor compound and H₂O₂ scavenging material so as to produce particulates with acceptable physical characteristics. The binder agents may be present at a level of from 0% to 40% by weight of the particulate. Preferably, the binder agents will be in intimate admixture with the organic peroxyacid bleach precursor compound and H₂O₂ scavenging material. Preferred binder agents have a melting point between 30°C-70°C or a substantial aqueous solubility. The binder agents are preferably present in amounts from 1-30% by weight of the particulate and most preferably from 5-20% by weight of the particulate.

Preferred binder agents include the C₁₀-C₂₀ alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole of alcohol and more preferably the C₁₅-C₂₀ primary alcohol ethoxylates containing from 20-100 moles of ethylene oxide per mole of alcohol. Preferred ethoxylates binder are tallow alcohol ethoxylated with 15 moles of ethylene oxide per mole of alcohol (TAE 25) and tallow alcohol ethoxylated with 50 moles of ethylene oxide per mole of alcohol (TAE 50).

Other preferred binder agents include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols with an average weight of from 600 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. Preferred binder of use herein is a copolymer of maleic acid/acrylic acid of Mw 70000. Also suitable is a homopolymer of acrylic acid. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C₁₀-C₂₀ alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole. Further examples of binder agents include the C₁₀-C₂₀ mono- and diglycerol ethers and also the C₁₀-C₂₀ fatty acids. Solutions of certain inorganic salts including sodium silicate are also of use for this purpose.

Cellulose derivatives including nonionic alkyl cellulose derivatives such as methylcellulose, carboxymethylcellulose, (hydroxypropyl methyl cellulose) and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acid or their salts are other examples of suitable binder agents.

The particulate can also include other components that are conventional in detergent compositions, provided that these are not incompatible *per se*. Example of such components include lime soap dispersants and fillers. The bleach precursor particulate may further be provided with a coating material. Said coating material may be selected from polyacrylic acid, cellulose acetate, co-polymeric polycarboxylic acid and monomeric aliphatic carboxylic acids such as citric acid. An exemplary disclosure is given in EP 382464 and WO92/13798. Such components and their levels of incorporation are described hereinafter but the total level of the components normally lies in the range of from 5% to 50% by weight of the bleach precursor composition. The peroxyacid precursor(s) should preferably form the major component of the precursor composition, i.e. from 50% to 95% by weight of the particulate, preferably at least 55% by weight and most preferably at least 60% by weight thereof.

Where the bleach precursor particulate are provided with a coating material, a preferred optional component is a dusting agent used at a level of from 1% to 5% by weight, particularly for those compositions wherein said bleach precursor composition is in agglomerate form. This dusting component improves the flow of the precursor composition and preferably takes the form of a water-insoluble inorganic compound of particle size <50 micrometers, preferably 1-10 micrometers. Examples of such compounds include the synthetic zeolites and hydrophobic silicas. Application of the dusting agent can take place with or after the application of the coating material.

The peroxyacid bleach precursor compositions can be carried out in a number of ways using equipment known in the art and the process may take place in batch wise or continuous fashion. In a batch process, to make the preferred agglomerate embodiments of the invention, an Eirich or Lodige FM agglomeration is used whilst the continuous process can utilise a Shugi Mixer or a Lodige CB or KM mixer. A combination of the Lodige CB and KM mixers is preferred.

A preferred process for producing a detergent composition of the invention comprises the steps of:

- a)-preparing a peroxyacid bleach precursor agglomerate by mixing an organic peroxyacid bleach precursor compound with an H₂O₂ scavenging material, to which is thereafter mixed a binder material,
- b)-treating said agglomerates with a coating material,
- c)-drying said coated agglomerates, and
- d)-incorporating said dried coated agglomerates in a detergent composition containing a source of peroxide compounds.

Additional detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the laundering operation in which it is to be used.

The compositions of the invention may for example, be formulated as had and machine laundry detergent compositions, including laundry additive compositions and compositions suitable for use in the pretreatment of stained fabrics.

The compositions of the invention preferably contain one or more additional detergent components selected from surfactants, builders, organic polymeric compounds, additional enzymes, suds suppressors, lime soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors and brighteners.

Surfactant

The detergent compositions of the invention preferably contain as an additional detergent component a surfactant selected from anionic, cationic, nonionic ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation of surfactant are from 1% to 35% by weight, most preferably from 1% to 20% by weight.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

Essentially any anionic surfactants useful for deterative purposes can be included in the compositions. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate sulfonate, carboxylate and sarcosinate surfactants.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₈-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkytpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₈-C₁₈ alkyl sulfates which have been ethoxylated with from about 0.5 to about 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₈-C₁₈ alkyl sulfate which has been ethoxylated with from about 0.5 to about 20, preferably from about 0.5 to about 5, moles of ethylene oxide per molecule.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₈-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Anionic carboxylate surfactants suitable for use herein include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Preferred alkyl ethoxy carboxylates for use herein include those with the formula RO(CH₂CH₂O)_xCH₂COO⁻M⁺ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20 %, and the amount of material where x is greater than 7, is less than about 25 %, the average x is from about 2 to 4 when the average R is C₁₃ or less, and the average x is from about 3 to 10 when the average R is greater than C₁₃, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C₁₂ to C₁₈ alkyl group.

Alkyl polyethoxy polycarboxylate surfactants suitable for use herein include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, wherein at least one R_1 or R_2 is a succinic acid radical or hydroxysuccinic acid radical, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Anionic secondary soap surfactant

Preferred soap surfactants are secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. The secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in alkyl-substituted cyclohexyl carboxylates. The secondary soap surfactants should preferably contain no ether linkages, no ester linkages and no hydroxyl groups. There should preferably be no nitrogen atoms in the head-group (amphiphilic portion). The secondary soap surfactants usually contain 11-15 total carbon atoms, although slightly more (e.g., up to 16) can be tolerated, e.g. p-octyl benzoic acid.

The following general structures further illustrate some of the preferred secondary soap surfactants:

A. A highly preferred class of secondary soaps comprises the secondary carboxyl materials of the formula $R^3CH(R^4)COOM$, wherein R^3 is $CH_3(CH_2)_x$ and R^4 is $CH_3(CH_2)_y$, wherein y can be O or an integer from 1 to 4, x is an integer from 4 to 10 and the sum of (x + y) is 6-10, preferably 7-9, most preferably 8.

B. Another preferred class of secondary soaps comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R^5-R^6-COOM , wherein R^5 is C^7-C^{10} , preferably C^8-C^9 , alkyl or alkenyl and R^6 is a ring structure, such as benzene, cyclopentane and cyclohexane. (Note: R^5 can be in the ortho, meta or para position relative to the carboxyl on the ring.)

C. Still another preferred class of secondary soaps comprises secondary carboxyl compounds of the formula $CH_3(CHR)_k-(CH_2)_m-(CHR)_n-CH(COOM)(CHR)_o-(CH_2)_p-(CHR)_q-CH_3$, wherein each R is C_1-C_4 alkyl, wherein k, n, o, q are integers in the range of 0-8, provided that the total number of carbon atoms (including the carboxylate) is in the range of 10 to 18.

In each of the above formulas A, B and C, the species M can be any suitable, especially water-solubilizing, counterion. Especially preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R-CON(R^1)CH_2COOM$, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Nonionic surfactant

Essentially any anionic surfactants useful for deterative purposes can be included in the compositions. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein: R^1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferable C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain $C_{11}-C_{17}$ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycidyl.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 18 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C₈-C₁₈ fatty alcohols and C₈-C₁₈ mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C₁₀-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C₁₂-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula



wherein R₂ is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkyl(phenyl), and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3; t is from 0 to 10, preferably 0, and X is from 1.3 to 8, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose.

Nonionic fatty acid amide surfactant

Fatty acid amide surfactants suitable for use herein are those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

A suitable example of an alkyl amphocarboxylic acid for use herein is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Amine Oxide surfactant

Amine oxides useful herein include those compounds having the formula $R^3(OR^4)_xN^+(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 18 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide group containing from 1 to 3, preferably 1, ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{18} alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethyloctylamine oxide, diethyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyldodecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide, cetyl dimethylamine oxide, stearyl dimethylamine oxide, tallow dimethylamine oxide and dimethyl-2-hydroxyoctadecylamine oxide. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10} - C_{18} acylamido alkyl dimethylamine oxide.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Betaine surfactant

The betaines useful herein are those compounds having the formula $R(R^1)_2N^+R^2COO^-$ wherein R is a C_8 - C_{18} hydrocarbyl group, preferably a C_{10} - C_{16} alkyl group or C_{10} - C_{16} acylamido alkyl group, each R^1 is typically C_1 - C_3 alkyl, preferably methyl, and R^2 is a C_1 - C_6 hydrocarbyl group, preferably a C_1 - C_3 alkylene group, more preferably a C_1 - C_2 alkylene group. Examples of suitable betaines include coconut acylamidopropyl dimethyl betaine; hexadecyl dimethyl betaine; C_{12} - C_{14} acylamidopropyl betaine; C_8 - C_{14} acylamido hexyldiethyl betaine; 4[C_{14} - C_{18} acylmethylamidodiethylammonio]-1-carboxybutane; C_{16} - C_{18} acylamidodimethyl betaine; C_{12} - C_{16} acylamidopentanedithyl betaine; [C_{12} - C_{16} acylmethylamidodimethyl betaine. Preferred betaines are C_{12} - C_{18} dimethyl-ammonio hexanoate and the C_{10} - C_{18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Sultaine surfactant

The sultaines useful herein are those compounds having the formula $(R(R^1)_2N^+R^2SO_3^-)$ wherein R is a C_8 - C_{18} hydrocarbyl group, preferably a C_{10} - C_{16} alkyl group, more preferably a C_{12} - C_{13} alkyl group, each R^1 is typically C_1 - C_3 alkyl, preferably methyl, and R^2 is a C_1 - C_6 hydrocarbyl group, preferably a C_1 - C_3 alkylene or, preferably, hydroxyalkylene group.

Ampholytic surfactant

Ampholytic surfactants can be incorporated into the detergent compositions herein. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched.

Cationic surfactants

Cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_8 - C_{16} , preferably C_8 - C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Water-soluble builder compound

The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, silicates and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadiene pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less than about 50°C, especially less than about 40°C.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Specific examples of water-soluble phosphate builders are the alkali metal triphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Suitable silicates include the water soluble sodium silicates with an SiO_2 : Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2 : Na_2O ratio of 2.0 is the most preferred silicate.

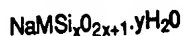
Silicates are preferably present in the detergent compositions in accord with the invention at a level of from 5% to 50% by weight of the composition, more preferably from 10% to 40% by weight.

Partially soluble or insoluble builder compound

The detergent compositions of the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of partially water soluble builders include the crystalline layered silicates. Examples of largely water insoluble builders include the sodium aluminosilicates.

Crystalline layered sodium silicates have the general formula

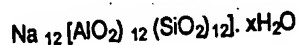


wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. The most preferred material is $\delta\text{-Na}_2\text{Si}_2\text{O}_5$, available from Hoechst AG as NaSKS-6.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof.

Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y]\cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{88}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}]\cdot 276\text{H}_2\text{O}$.

Heavy metal ion sequestrant

The detergent compositions of the invention may preferably contain a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions, especially alter the first stages of dissolution/dispersion of the peroxyacid bleach precursor. For this purpose, the heavy metal ion sequestrant will be present in the detergent composition as a component separate from the peroxyacid bleach precursor composition. These heavy metal ion sequestrants may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least

1:1.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate), hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_3EDDS . Examples of such preferred magnesium complexes of EDDS include MgEDDS and Mg_2EDDS .

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133.

The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

5 EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequesterant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS) is also suitable.

10 Bleach catalyst

The compositions optionally contain a transition metal containing bleach catalyst.

One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, 15 such as zinc or aluminum cations, and a sequesterant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_8(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

25 The bleach catalysts useful in the compositions herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})(\text{OCH}_3)_3(\text{PF}_6)$.

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:

35



45 wherein R^1 , R^2 , R^3 , and R^4 can each be selected from H, substituted alkyl and aryl groups such that each $\text{R}^1\text{-N}=\text{C}-\text{R}^2$ and $\text{R}^3\text{-C}=\text{N}-\text{R}^4$ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR^5R^6 , NR^7 and $\text{C}=\text{O}$, wherein R^5 , R^6 , and R^7 can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. 50 Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe, bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include $\text{Co}(2,2'\text{-bispyridylamine})\text{Cl}_2$, $\text{Di}(\text{isothiocyanato})\text{bispyridylamine-cobalt (II)}$, $\text{tris}(\text{dipyridylamine-cobalt(II)})$ perchlorate, $\text{Co}(2,2'\text{-bispyridylamine})_2\text{O}_2\text{ClO}_4$, $\text{Bis}(2,2'\text{-bispyridylamine})$ copper(II) perchlorate, $\text{tris}(\text{di-2-pyridylamine})$ iron(II) perchlorate, and mixtures thereof.

Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metalloporphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manga-

nese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

The bleach catalyst is typically used in a catalytically effective amount in the compositions and processes herein. By "catalytically effective amount" is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance bleaching and removal of the stain or stains of interest from the target substrate. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some users elect to use very hot water; others use warm or even cold water in laundering operations. Of course, the catalytic performance of the bleach catalyst will be affected by such considerations, and the levels of bleach catalyst used in fully-formulated detergent and bleach compositions can be appropriately adjusted. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 1 ppm to about 200 ppm of the catalyst species in the wash liquor. To illustrate this point further, on the order of 3 micromolar manganese catalyst is effective at 40°C, pH 10 under European conditions using perborate and a bleach precursor. An increase in concentration of 3-5 fold may be required under U.S. conditions to achieve the same results.

Enzyme

Another preferred ingredient useful in the detergent compositions is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of *B. licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme (lipase) may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp. including *Pseudomonas pseudoalcaligenes* or *Pseudomonas fluorescens*. Lipase from chemically or genetically modified mutants of these strains are also useful herein.

A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from *Humicola lanuginosa* and expressing the gene in *Aspergillus oryza*, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, but excluding any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-10,000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

Other suitable organic polymeric compounds include the copolymers of acrylamide and acrylate having a molecular weight of from 3,000 to 100,000, and the acrylate/fumarate copolymers having a molecular weight of from 2,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Suds suppressing system

The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl and alkanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

Copolymers of ethylene oxide and propylene oxide, particularly the mixed ethoxylated/propoxylated fatty alcohols with an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10, are also suitable antifoam compounds for use herein.

Suitable 2-alkyl-alkanols antifoam compounds for use herein have been described in DE 40 21 265. The 2-alkyl-alkanols suitable for use herein consist of a C₈ to C₁₈ alkyl chain carrying a terminal hydroxy group, and said alkyl chain is substituted in the α position by a C₁ to C₁₀ alkyl chain. Mixtures of 2-alkyl-alkanols can be used in the compositions according to the present invention.

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to

10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Coming under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A preferred particulate suds suppressor system useful herein comprises a mixture of an alkylated siloxane of the type hereinabove disclosed and solid silica.

The solid silica can be a fumed silica, a precipitated silica or a silica, made by the gel formation technique. The silica particles suitable have an average particle size of from 0.1 to 50 micrometers, preferably from 1 to 20 micrometers and a surface area of at least 50m²/g. These silica particles can be rendered hydrophobic by treating them with dialkylsilyl groups and/or trialkylsilyl groups either bonded directly onto the silica or by means of a silicone resin. It is preferred to employ a silica the particles of which have been rendered hydrophobic with dimethyl and/or trimethyl silyl groups. A preferred particulate antifoam compound for inclusion in the detergent compositions in accordance with the invention suitably contain an amount of silica such that the weight ratio of silica to silicone lies in the range from 1:100 to 3:10, preferably from 1:50 to 1:7.

Another suitable particulate suds suppressing system is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Other highly preferred particulate suds suppressing systems are described in copending European Application 91870007.1 in the name of the Procter and Gamble Company which systems comprise silicone antifoam compound, a carrier material, an organic coating material and glycerol at a weight ratio of glycerol : silicone antifoam compound of 1:2 to 3:1. Copending European Application 91201342.0 also discloses highly preferred particulate suds suppressing systems comprising silicone antifoam compound, a carrier material, an organic coating material and crystalline or amorphous aluminosilicate at a weight ratio of aluminosilicate : silicone antifoam compound of 1:3 to 3:1. The preferred carrier material in both of the above described highly preferred granular suds controlling agents is starch.

An exemplary particulate suds suppressing system for use herein is a particulate agglomerate component, made by an agglomeration process, comprising in combination

(i) from 5% to 30%, preferably from 8% to 15% by weight of the component of silicone antifoam compound, preferably comprising in combination polydimethyl siloxane and silica;

(ii) from 50% to 90%, preferably from 60% to 80% by weight of the component, of carrier material, preferably starch;

(iii) from 5% to 30%, preferably from 10% to 20% by weight of the component of agglomerate binder compound, where herein such compound can be any compound, or mixtures thereof typically employed as binders for agglomerates, most preferably said agglomerate binder compound comprises a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 50 to 100; and

(iv) from 2% to 15%, preferably from 3% to 10%, by weight of C₁₂-C₂₂ hydrogenated fatty acid.

Clay flocculating agent

The compositions of the invention may contain a clay flocculating agent, preferably present at a level of from 0.005% to 10%, more preferably from 0.05% to 5%, most preferably from 0.1% to 2% by weight of the composition.

The weight ratio of clay mineral compound to clay flocculating agent is preferably from 300:1 to 1:1, more preferably from 80:1 to 10:1, most preferably from 60:1 to 20:1.

The clay flocculating agent functions such as to bring together the particles of clay compound in the wash solution and hence to aid their deposition onto the surface of the fabrics in the wash. This functional requirement is hence different from that of clay dispersant compounds which are commonly added to laundry detergent compositions to aid the removal of clay soils from fabrics and enable their dispersion within the wash solution.

Preferred as clay flocculating agents herein are organic polymeric materials having an average weight of from 100,000 to 10,000,000, preferably from 150,000 to 5,000,000, more preferably from 200,000 to 2,000,000.

Suitable organic polymeric materials comprise homopolymers or copolymers containing monomeric units selected from alkylene oxide, particularly ethylene oxide, acrylamide, acrylic acid, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Homopolymers of ethylene oxide, acrylamide and acrylic acid are preferred.

European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe preferred organic polymeric clay flocculating agents for use herein.

Inorganic clay flocculating agents are also suitable herein, typical examples of which include lime and alum.

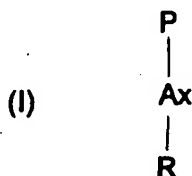
10 Polymeric dye transfer inhibiting agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

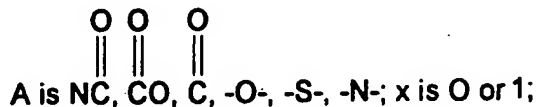
The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula:

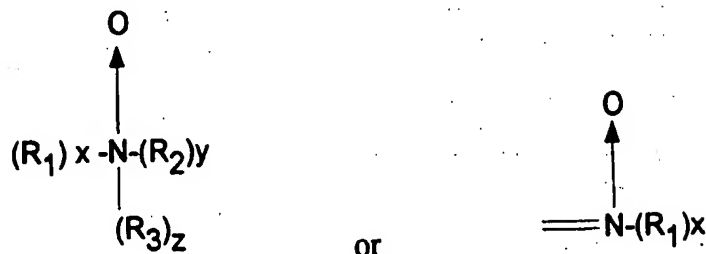


wherein P is a polymerisable unit, whereto the R-N-O group can be attached to, or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.



R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R₁, R₂, and R₃ are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides where to the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PK_a < 10, preferably PK_a < 7, more preferred PK_a < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Preferred polymers for use herein may comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000. The preferred N-vinylimidazole N-vinylpyrrolidone copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4.

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilise polyvinylpyrrolidone "PVP" having an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

Polyvinylpyrrolidone may be incorporated in the detergent compositions herein at a level of from 0.01% to 5% by weight of the detergent, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylpyrrolidone delivered in the wash solution is preferably from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

d) Polyvinylloxazolidone

The detergent compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinylloxazolidone incorporated in the detergent compositions may be from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylloxazolidone delivered in the wash solution is typically from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

e) Polyvinylimidazole

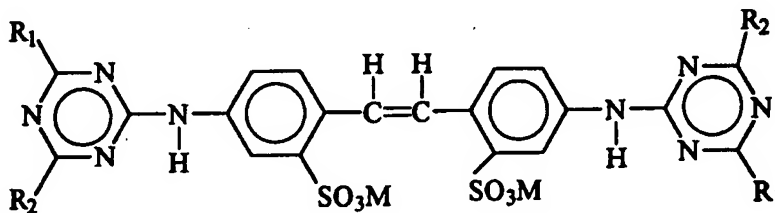
The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinylimidazole incorporated in the detergent compositions may be from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylimidazole delivered in the wash solution is from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

Optical brightener

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morpholino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This

particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino] 2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. These may be present as distinct components or as components of the, hereinbefore described, hydrophobically activated clay materials. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

Form of the compositions

The detergent compositions of the invention can be formulated in any desirable form such as powders, granulates, pastes, and tablets.

The particle size of the components of granular compositions in accordance with the invention should preferably be such that no more than 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 450 g/litre, more usually at least 600 g/litre and more preferably from 650 g/litre to 1200 g/litre.

Making processes - granular compositions

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

Laundry washing methods

The compositions of the invention may be used in essentially any washing or cleaning method, including handwash, soaking and machine laundry washing methods.

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition

in accord with the invention. The detergent can be added to the wash solution either via the dispenser drawer of the washing machine or by a dispensing device. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

5 In a preferred washing method herein a dispensing device containing an effective amount of detergent product is introduced into the drum of a front-loading washing machine before the commencement of the wash cycle.

The dispensing device is a container for the detergent product which is used to deliver the product directly into the drum of the washing machine. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

10 Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its immersion in the wash water.

15 To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

20 Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use in accord with the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly known as the "granulette".

25 Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

30 Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

Packaging for the compositions

45 Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in copending European Application No. 93970141.4.

Abbreviations used in Examples

50 In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS : Sodium linear C12 alkyl benzene sulphonate

TAS : Sodium tallow alcohol sulphate

55 XYAS : Sodium C_{1X}-C_{1Y} alkyl sulfate

25EY : A C₁₂₋₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide

XYEZ	: A C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of Z moles of ethylene oxide
5 XEYZS	: C _{1x} -C _{1y} sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole
QAS	: R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ -C ₁₄
10 Soap	: Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and a coconut oils.
TFAA	: C ₁₆ -C ₁₈ alkyl N-methyl glucamide.
Silicate	: Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio = 2.0)
15 NaSKS-6	: Crystalline layered silicate of formula δ-Na ₂ Si ₂ O ₅
Bicarbonate	: Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm
20 Carbonate	: Anhydrous sodium carbonate
MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
STPP	: Anhydrous sodium tripolyphosphate
25 Zeolite A	: Hydrated Sodium Aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ . 27H ₂ O having a primary particle size in the range from 1 to 10 micrometers
Citric acid	: Anhydrous citric acid
30 Citrate	: Tri-sodium citrate dihydrate
Percarbonate	: Anhydrous sodium percarbonate bleach coated with a coating of sodium silicate (Si ₂ O:Na ₂ O ratio = 2:1) at a weight ratio of percarbonate to sodium silicate of 39:1
35 PB1	: Anhydrous sodium perborate bleach of nominal formula NaBO ₂ .H ₂ O ₂
PB4	: Sodium perborate tetrahydrate of nominal formula NaBO ₂ .3H ₂ O.H ₂ O ₂
40 TAED	: Tetraacetylenediamine particle formed by agglomerating TAED with a copolymer of 1:4 maleic/acrylic acid having an average molecular weight of about 70,000 at weight ratio of TAED:copolymer of 85:10, and then coating said agglomerate with a coating of said copolymer at a weight ratio of agglomerate:coating of 95:5.
45 NOBS	: Nonaoyloxybenzene sulfonate in the form of the sodium salt.
Protease	: Proteolytic enzyme sold under the tradename Savinase by Novo Industries A/S with an activity of 13 KNPU/g.
50 Protease #	: Proteolytic enzyme sold under the tradename Savinase by Novo Industries A/S with an activity of 4 KNPU/g.
Protease # #	: Proteolytic enzyme sold under the tradename FN3 by Genencor.
55 Alcalase	: Proteolytic enzyme sold Novo Industries A/S with an activity of 3 AU/g.
Amylase	: Amylolytic enzyme sold under the tradename Termamyl 60T by Novo Industries A/S with an activity of 300 KNU/g

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	Amylase #	: Amylolytic enzyme sold under the tradename Termamyl 120T by Novo Industries A/S with an activity of 600 KNU/g
	Cellulase	: Cellulosic enzyme sold by Novo Industries A/S with an activity of 1000 CEVU/g
5	Lipase	: Lipolytic enzyme sold under the tradename Lipolase by Novo Industries A/S with an activity of 165 KLU/g
	Endolase	: Endoglucanase A sold by Novo Industries A/S
10	CMC	: Sodium carboxymethyl cellulose
	DETPMP	: Diethylene triamine penta (Methylene phosphonic acid), marketed by Monsanto under the Tradename Dequest 2060
15	HEDP	: Hydroxy-ethane 1,1 diphosphonic acid
	EDDS	: Ethylenediamine -N, N'- disuccinic acid, [S,S] isomer in the form of the sodium salt
20	PVNO	: Poly (4-vinylpyridine)-N-oxide copolymer of vinylimidazole and vinylpyrrolidone having an average molecular weight of 10,000.
	PVPVI	: Copolymer of polyvinylpyrrolidone and vinylimidazole
25	Clay	: Calcium montmorillonite sold by Colin Stewart Minchem Ltd and containing 50 ppm of Cu, 8000 ppm Fe and 80 ppm Mn.
	Acid Clay	: Calcium montmorillonite treated with an organic acid sold by Sud Chemie AG
30	Granular Suds Suppressor	: 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form
	SRA (Soil Release Agents)	: Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
	Metolose	: Carboxy methoxy ether
35	Sulphate	: Anhydrous sodium sulphate
	Brightener 1	: Disodium 4,4'-bis(2-sulphostyryl)biphenyl
40	Brightener 2	: Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2,2'-disulphonate.
	Photoactivated bleach	: Sulphonated Zinc Phthalocyanine encapsulated in dextrin soluble polymer
45	Silicone antifoam	: Polydimethylsiloxane foam controller with Siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

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Example 1

An agglomerate having the following formulation was made in an Eirich Mixer model RV02 (tradename)

	wt%
TAED	85
Clay**	5
MA/AA* of MWt 70,000	10
	100

*supplied as Sokolan 45 (trade name) ex BASF

**of the Bentonite type ex Colin Stewart Minchem Ltd and containing 8000 ppm of Fe, 50 ppm Cu and 80 ppm Mn.

The TAED and the clay were added to the Eirich mixer and pre-mixed. The temperature of the powder was 25°C. An aqueous solution of the MA/AA binder, which was at a temperature of 60°C, was added to the powder mix, with the Eirich blades and pan rotating, over a period of 30 seconds. The resulting mass was further mixed for 30 seconds. The mixing was then stopped and the agglomerate product removed from the Eirich mixer and further dried in a fluid bed dryer to a moisture content of 2%. The product was then sieved and materials that were greater than 1180 micrometers and smaller than 250 micrometers were removed.

Example 2

The same procedure as above was repeated with the exception of the clay being replaced in the same amounts with an acid clay of the Tonsil P type ex Sud Chemie AG.

Example 3

An agglomerate having the following formulation was made in an Eirich Mixer model RV02 (tradename)

	wt%
TAED	80
Clay**	5
MA/AA* of MWt 70,000	10
	95

*supplied as Sokolan 45 (trade name) ex BASF

** of the Bentonite type ex Colin Stewart Minchem Ltd and carrying 8000 ppm Fe, 50 ppm Cu and 80 ppm Mn

The TAED and the clay were added to the Eirich mixer and pre-mixed. The temperature of the powder was 25°C. The molten binder, which was at a temperature of 60°C, was added to the powder mix, with the Eirich blades and pan

rotating, over a period of 30 seconds. The resulting mass was further mixed for 30 seconds. The mixing was then stopped and the agglomerate product removed from the Eirich mixer and further dried in a fluid bed dryer. The product was then sieved and materials that were greater than 1180 micrometers and smaller than 250 micrometers were removed. The resulting agglomerate was then coated with a MA/AA copolymer at a level of coating:agglomerate of 5:95.

Example 4

An agglomerate having the following formulation was made on a continuous dual Lodige process involving a CB Lodige high shear mixer, followed by a KM Lodige low shear mixer.

	wt%
TAED	75
Clay**	10
MA/AA* of MWt 70,000	10
	95

*supplied as Sokolan 45 (trade name) ex BASF

** of the Bentonite type ex Colin Stewart Minchem Ltd and carrying 8000 ppm Fe, 50 ppm Cu and 80 ppm Mn

The TAED and the clay were added continuously to the inlet port of the CB Lodige, the temperature of the powders being 25°C. The molten binder, which was at a temperature of 60°C, was also added continuously to the CB Lodige. The resulting mass was passed onto the KM Lodige for final size enlargement. The wet agglomerate product was then dried in a fluid bed dryer to reduce moisture to a desired value of 2%. The product was then sieved and materials that were greater than 1700 micrometers and smaller than 425 micrometers were removed. The resulting agglomerate was then coated with a MA/AA copolymer at a level of coating:agglomerate of 5:95 in a KM Lodige.

Example 5

The following laundry detergent compositions A, B, C, D and E were prepared, A and B are comparative compositions and C to E are in accord with the invention:

	A	B	C	D	E
45AS/25AS (3:1)	9.1	9.1	9.1	9.1	9.1
35AE3S	2.3	2.3	2.3	2.3	2.3
24E5	4.5	4.5	4.5	4.5	4.5
TFAA	2.0	2.0	2.0	2.0	2.0
Zeolite A	10.2	10.2	10.2	10.2	10.2
Na SKS-6/citric acid (79:21)	10.6	10.6	10.6	10.6	10.6
Carbonate	7.6	7.6	7.6	7.6	7.6
TAED	5	6.67	-	-	-
TAED/Clay particle (1)	-	-	6.67	-	-
TAED/Clay particle (2)	-	-	-	6.67	-
TAED/Clay particle (3)	-	-	-	-	6.67
Percarbonate	22.5	22.5	22.5	22.5	22.5
DETPMP	0.5	0.5	0.5	0.5	0.5
Protease	0.55	0.55	0.55	0.55	0.55
Lipase	0.15	0.15	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28	0.28	0.28
Amylase	0.27	0.27	0.27	0.27	0.27
Polycarboxylate	3.1	3.1	3.1	3.1	3.1
CMC	0.4	0.4	0.4	0.4	0.4
PVNO	0.03	0.03	0.03	0.03	0.03
Granular suds suppressor	1.5	1.5	1.5	1.5	1.5
Minors/misc to 100%					
* (1) as in Example 1 (2) as in Example 2 (3) as in Example 3					

Example 5 - Comparative Performance Testing

Test protocol 1 - patchy fabric discolouration testing

The formulations A to E were subjected to a full scale washing machine test using 12 Miele automatic washing machine (Model WM W698) set to the short wash cycle at 40°C for each formulation. Water of 12° German hardness (= 1.8 mol Ca²⁺/litre) was used. The fabric swatches to be placed in the washing machines by pairs were numbered from 1 to 24 and made from garments obtained from High Street stores as detailed below:

Swatch s Number	Type of Garnment	Colour	Type of fabric
1&4	Wool Cardigan	Navy Blue	50/50% Wool/Acrylic
2&3	Mens' Shirt	Dark green	100% Cotton
5&8	Tee Shirt	Black	100% Cotton
6&7	Mens Sweat Shirt	Black	10/90% Cotton/polyest er
9&12	Tee Shirt	Black	100% Cotton
10&11	Denim Shirt	Navy	100% Cotton
13&16	Long sleeve sweatshirt	Black	50/50% Cotton/ polyester
14&15	Jeans	Black	100% Cotton
17&20	Mens' Trousers	Black	65/35% Polyester /viscose
18&19	Mens' Cord Shirt	Green	100% Cotton
21&24	Mens' Shirt	Dark green	100% Cotton
22&23	Leggings	Black	97/3% Cotton/Lycra

Each machine was loaded with a ballast of 4lbs (approx. 1.9kg) of clean sheets, with on top of it the following materials: a fabric swatch, 100g of the formulation dispensed from a granulette dispensing device, of the type disclosed in EP-A-343,070 and commonly supplied for use with the Ariel Ultra (tradename) granular laundry detergent as sold by The Procter and Gamble Company and a second fabric swatch on top of it. The swatches of 30cmx30cm were folded together so as to cause entrapment of the granulette during the first stages of dissolution/dispersion of the detergent composition containing the bleach precursor composition. At the end of the cycle, the swatches were retrieved and dried in the open air.

The swatches were then graded visually for fabric discolouration using a grading system.

Three coloured swatches demonstrating differing degrees of patchy fabric colour damage are used as standards to establish a 6 point scale in which 0 represents 'no discolouration' and 5 represents 'extreme discolouration'. The three standards are used to define the mid points between the various descriptions of discolouration, viz

- 0 no discolouration
- 1 very slight discolouration
- 2 slight discolouration
- 3 clearly noticeable discolouration
- 4 very discoloured
- 5 extreme discolouration

Two expert panellists are used and their results are averaged.

Comparative testing 1 - patchy fabric discolouration

Using the above test protocol 1 to compare patchy fabric discolouration resulting from use of formulations A to E the following results were obtained

% of swatches having grade							
Formulation	0	1	2	3	4	5	Overall Grade
A	67	17	8	8	0	0	0.57
B	58	13	13	12	4	0	0.91
C	84	0	8	8	0	0	0.40
D	80	4	4	12	0	0	0.48
E	75	4	8	13	0	0	0.59

It can be seen that formulations C to E in accordance with the invention produce appreciably less patchy fabric discolouration than formulations A and B not in accordance with the invention.

Test protocol 2 - stain removal

Three white cotton sheets were prewashed in a non-biological bleach-free heavy duty detergent. Tea stains were then applied to one sheet, wine stains to the second sheet and coffee stains to the third one. Sets of six test swatches of size 6cm x 6cm were cut from each sheet.

The sets of fabric swatches were subjected to one wash cycle in an automatic washing machine. The swatches were then assessed for removal of the tea, wine and coffee stains using a well-established lightness measurement method.

In more detail, a Miele 756 WM automatic washing machine was employed, and the 40°C short cycle programme selected. Water of 12° German hardness (= 1.8 mol Ca²⁺/litre) was used. 100g of detergent, dispensed from a granulette dispensing device was employed. One swatch of each fabric type was washed along with a ballast load of 4lbs (approx 1.9Kg) of lightly soiled sheets.

Stain removal was assessed by making LAB (lightness) measurements using the X-rite (tradename) colour eye spectrophotometer. An unstained cotton sheet was used as the reference. A stain removal index, ΔR , was calculated as follows:

$$\Delta R = (L_{\text{washed}} - L_{\text{unwashed}}) / (L_{\text{unwashed}} - L_{\text{reference}}) \times 100$$

where differences of ΔR below 4% are not significant.

Comparative testing 2 - stain removal

The above test protocol 2 was followed in comparing the efficiency of Compositions B and C in removing different type of bleach sensitive stains. The results obtained were as follows:

ΔR (%)	B	C
Tea	78	76
Wine	82	83
Coffee	75	74

The stain removal obtained for each of Compositions B and C is shown to be comparable. Thus the presence of HMI as an H₂O₂ scavenger, and carried in a clay, in Composition C does not significantly compromise the stain removal capacity of that Composition versus that of Composition B. The perhydrolysis performance of the bleach precursor is also seen not to be significantly compromised.

Example 6

The following laundry detergent compositions F to J in accord with the invention were prepared:

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	F	G	H	I	J
LAS	2.0	2.0	2.0	2.0	2.0
TAS	0.5	0.5	0.5	0.5	0.5
45AS	6.0	6.0	6.0	6.0	6.0
25E3S	2.0	2.0	2.0	2.0	2.0
24E5	5.0	5.0	5.0	5.0	5.0
TFAA	2.0	2.0	2.0	2.0	2.0
Zeolite A	15.0	15.0	15.0	15.0	15.0
Citric acid	2.0	2.0	2.0	2.0	2.0
NaSKS-6	9.0	9.0	9.0	9.0	9.0
Carbonate	14	14	14	14	14
Silicate	2.0	2.0	2.0	2.0	2.0
Sulphate	6.0	6.0	6.0	6.0	6.0
MA/AA	3.0	3.0	3.0	3.0	3.0
CMC	0.3	0.3	0.3	0.3	0.3
SRA	0.15	0.15	0.15	0.15	0.15
Metolose	0.5	0.5	0.5	0.5	0.5
PVNO/PVPVI	0.02	0.02	0.02	0.02	0.02
Cellulase	0.5	0.5	0.5	0.5	0.5
Amylase #	0.2	0.2	0.2	0.2	0.2
Lipase	0.1	0.1	0.1	0.1	0.1
Protease # #	0.4	0.4	0.4	0.4	0.4
TAED/Clay particle (1)	-	-	4.5	-	-
TAED/Clay particle (2)	-	-	-	4.5	-
TAED/Clay particle (3)	-	-	-	-	4.5
TAED/Clay particle (4)	4.5	4.5	-	-	-
DETPMP	0.4	-	-	-	-
MgSO ₄	0.3	0.3	0.3	0.3	0.3
Percarbonate	18.0	18.0	18.0	18.0	18.0
HEDP	0.5	0.5	0.5	0.5	0.5
EDDS	-	0.3	0.3	0.3	0.3
Brightener 1	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach	0.003	0.003	0.003	0.003	0.003
Granular Suds Suppressor	0.3	0.3	0.3	0.3	0.3
Perfume	0.3	0.3	0.3	0.3	0.3

Continuation of the Table on the next page

TOTAL	100	100	100	100	100
* (1) as in Example 1 (2) as in Example 2 (3) as in Example 3 (4) as in Example 4					

Example 7

The following detergent formulations, according to the present invention were prepared, where formulation K is a phosphorus-containing detergent composition, formulation L is a zeolite-containing detergent composition and formulation M is a compact detergent composition:

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	K	L	M
Blown Powder			
STPP	24.0	-	24.0
Zeolite A	-	24.0	-
Sulphate	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DETPMP	0.4	0.4	0.2
Spray On			
45E7	2.5	2.5	2.0
25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10
PB1	4.0	4.0	-
TAED (4)	3.0	3.0	1.0
Photoactivated bleach	0.02%	0.02%	0.02%
Protease#	1.0	1.0	1.0
Lipolase	0.4	0.4	0.4
Termamyl	0.25	0.30	0.15
Sulphate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670
* (4) as in Example 4			

Example 8

The following detergent formulations N and O, according to the present invention were prepared:

	N	O
Blown Powder		
Zeolite A	22.0	6.0
Sulphate	10.0	7.0
MA/AA	3.0	6.0
LAS	12.0	22.0
45AS	7.0	7.0
Silicate	1.0	5.0
Soap	-	2.0
Brightener 1	0.2	0.2
Carbonate	16.0	20.0
DETPMP	0.4	0.4
Spray On		
45E7	1.0	1.0
Dry additives		
PVPV/PVNO	0.5	0.5
Protease #	1.0	1.0
Lipolase	0.4	0.4
Termamyl	0.1	0.1
Carezyme	0.1	0.1
NOBS (4)	6.1	4.5
PB1	5.0	6.0
Sulphate	6.0	-
Balance (Moisture and Miscellaneous)	100	100
* (4) as made in Example 4, wherein TAED is replaced by NOBS		

Example 9

The following high density and bleach-containing detergent formulations P and Q, according to the present invention were prepared:

	P	Q
Blown Powder		
Zeolite A	15.0	15.0
Sulphate	-	5.0
LAS	3.0	3.0
QAS	-	1.5
DETPMP	0.4	0.4
CMC	0.4	0.4
MA/AA	4.0	2.0
Agglomerates		
LAS	5.0	5.0
TAS	2.0	2.0
Silicate	3.0	3.0
Zeolite A	8.0	8.0
Carbonate	8.0	8.0
Spray On		
Perfume	0.3	0.3
45E7	2.0	2.0
25E3	2.0	-
Dry additives		
Citrate	5.0	-
Bicarbonate	-	3.0
Carbonate	8.0	15.0
TAED (4)	6.0	2.0
PB1	14.0	7.0
Protease #	1.0	1.0
Lipolase	0.4	0.4
Termamyl	0.6	0.6
Carezyme	0.6	0.6
Silicone antifoam granule	5.0	5.0
Sulphate	-	3.0
Balance (Moisture and Miscellaneous)	100.0	100.0
Density (g/litre)	850	850
(4) as in Example 4		

Example 10

The following high density detergent formulations R and S, according to the present invention were prepared:

	R	S
Agglomerate		
45AS	11.0	14.0
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DETPMP	0.4	0.4
Metolose	0.6	0.2
Spray On		
25E5	5.0	5.0
Perfume	0.5	0.5
Dry Additives		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED (4)	5.0	7.0
Percarbonate	20.0	20.0
SRA	0.3	0.3
Protease #	1.4	1.4
Lipolase	0.4	0.4
Carezyme	0.6	0.6
Termamyl	0.6	0.6
Silicone antifoam particle	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850
* (4) as in Example 4		

Claims

1. A detergent composition containing:

- (a) a source of peroxide compounds
- (b) a peroxyacid bleach precursor composition comprising

- i) an organic peroxyacid bleach precursor compound,
- ii) an H_2O_2 scavenging material,

5 wherein said organic peroxyacid bleach precursor compound and said H_2O_2 scavenging material are in close physical proximity within said composition.

2. A detergent composition according to Claim 1, wherein said organic peroxyacid bleach precursor compound are in intimate admixture within said composition.
- 10 3. A detergent composition according to either one of Claim 1 or 2, wherein said H_2O_2 scavenger is selected from compounds reacting with H_2O_2 via a decomposition, a neutralisation or adsorption process or any combination thereof.
- 15 4. A detergent composition according to any one of Claim 1-3, wherein said H_2O_2 scavenger is selected from a heavy metal ion, a catalase enzyme and a peroxydase enzyme.
5. A detergent composition according to any one of Claim 1-4, wherein said H_2O_2 scavenger is an heavy metal ion selected from elements contained in the third and fourth rows of the third to the twelfth columns of the periodic table.
- 20 6. A detergent composition according to either one of Claim 4 or 5, wherein said heavy metal ion is selected from Fe, Cu and Mn and mixtures thereof.
7. A detergent composition according to any one of Claim 4-6, wherein said heavy metal ion is in amount less than 5% by weight of the bleach precursor composition, preferably less than 1%, more preferably less than 0.1%.
- 25 8. A detergent composition according to any one of Claim 1-4, wherein said H_2O_2 scavenger is an enzyme of the catalase-type selected from Terminox® and Fermocolase®.
9. A detergent composition according to any one of Claim 1-4, wherein said H_2O_2 scavenger is an enzyme of the peroxidase-type selected from horseradish peroxidase, ligninase and haloperoxidase.
- 30 10. A detergent composition according to either one of Claim 8 or 9, wherein said enzyme is in amount less than 5% by weight of the bleach precursor composition.
- 35 11. A detergent composition according to any one of Claim 4-7, wherein said heavy metal ion is carried in a mineral material containing at least 200 ppm of said heavy metal ion.
12. A detergent composition according to Claim 11, wherein said mineral material is a non three dimensional phyllosilicate mineral material.
- 40 13. A detergent composition according to either one of Claim 11 or 12, wherein said mineral material is a clay.
14. A detergent composition according to any one of Claims 11-13, wherein said mineral material is a smectite clay.
- 45 15. A detergent composition according to any one of Claim 1-14, wherein said bleach precursor is present at a level of greater than 3% by weight of the detergent composition.
16. A detergent composition according to any one of Claim 1-15, wherein said bleach precursor is selected from those containing one or more N- or O-acyl groups.
- 50 17. A detergent composition according to Claim 16, wherein said bleach precursor is N,N',N' tetra acetyl ethylene diamine.
18. A detergent composition according to any one of Claim 1-17, wherein said bleach precursor composition is an agglomerate further bound with a binder.
- 55 19. A detergent composition according to Claim 18, wherein said bleach precursor agglomerate is further provided with a coating material.

20. A detergent composition according to Claim 19, wherein said coating material is selected from polyacrylic acid, cellulose acetate, copolymeric polycarboxylic acid and monomeric aliphatic carboxylic acid and mixtures thereof.
- 5 21. A detergent composition according to any one of Claims 1-20, wherein said source of active oxygen is an hydrogen peroxide source, preferably an inorganic perhydrate bleach.
22. A detergent composition according to Claims 21, wherein said perhydrate bleach is sodium perborate or sodium percarbonate.
- 10 23. A detergent composition according to any one of Claims 1-22, comprising a surfactant material and further incorporating a heavy metal ion sequestrant, the latter being selected from organic phosphonates, nitrilotriacetic acid and polyaminocarboxylic acids.
- 15 24. A detergent composition according to Claim 23, wherein said heavy metal ion sequestrant is ethylenediamine disuccinate (EDDS).
25. A detergent composition according to either one of Claim 23 or 24, wherein said heavy metal ion sequestrant is present as a component separate from said peroxyacid bleach precursor composition.
- 20 26. A process for producing a detergent composition as defined in any one of Claims 1-25, comprising the steps of:
- a)-preparing a peroxyacid bleach precursor agglomerate by mixing an organic peroxyacid bleach precursor compound with an H_2O_2 scavenging material, to which is thereafter mixed a binder material,
 - 25 b)-treating said agglomerates with a coating material,
 - c)-drying said coated agglomerates, and
 - d)-incorporating said dried coated agglomerates in a detergent composition containing a source of peroxide compounds.